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7. SILICON TETRAISOTHIOCYANATE AND METHYLSILICON ISOTHIOCYANATES

$$SiCl_4 + 4NH_4SCN \rightarrow Si(NCS)_4 + 4NH_4Cl$$

$$(CH_3)_nSiCl_{4-n} + (4 - n)NH_4SCN \rightarrow (CH_3)_nSi(NCS)_{4-n} + (4 - n)NH_4Cl \quad (n = 1, 2, \text{or } 3)$$

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Silicon tetraisothiocyanate was first prepared by Miquel[1,2] and Reynolds[3] by treating silicon(IV) chloride with lead thiocyanate. Later, Forbes and Anderson[4–9] prepared many substituted silicon isothiocyanates by metathetical reaction of the corresponding chlorosilanes with silver thiocyanate. On the bases of molecular refraction studies, the latter workers concluded that the silane derivatives are isothiocyanates rather than the isomeric thiocyanates. Conclusive proof that these compounds are isothiocyanates is their formation in good yield from isocyanosilanes and sulfur:[10]

$$R_3SiNC + S \rightarrow R_3SiNCS$$

Although the silicon isothiocyanates have been prepared by treating chlorosilanes with the thiocyanates of sodium,

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potassium, ammonium, silver, lead, and copper, the best yields are obtained with silver thiocyanate or ammonium thiocyanate.[11] Procedures describing the use of these two salts are given below. Ammonium thiocyanate gives approximately 5% lower yields of the silicon isothiocyanates, whereas the silver salt gives less pure products.

Procedures for the corresponding cyanate compounds are described in synthesis 6.

Procedure

A. SILVER THIOCYANATE

A solution of 457 g. (6.0 mols) of ammonium thiocyanate in 1 l. of distilled water is added over a 15-minute period, with good stirring, to a solution of 1019 g. (6.0 mols) of silver nitrate in 1 l. of distilled water. The temperature is maintained below 25° by cooling the mixture in an ice bath. The precipitate is filtered through a sintered-glass funnel, washed with five 70-ml. portions of distilled water followed by two 50-ml. portions of acetone, pressed thoroughly, and drained. The white solid is then spread on a large polyethylene tray, covered loosely by aluminum foil to prevent decomposition by light, and dried overnight by exposure to a rapid stream of air *in a good hood.* Residual moisture is removed by placing the product in a crystallizing dish in a vacuum desiccator covered by aluminum foil and evacuating for 3 hours.

B. SILICON TETRAISOTHIOCYANATE

Finely powdered ammonium thiocyanate (190 g.; 2.5 mols; 25% theoretical excess) is mixed with 800 ml. of anhydrous sodium-dried benzene* contained in a 2-l. three-necked standard-taper flask fitted with a motor-driven stirrer, a thermometer, a 125-ml. dropping funnel, and a

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* If less benzene is employed, the resulting silicon isothiocyanate crystallizes, thus making separation of ammonium salts difficult.

300-mm. Allihn condenser equipped with a Drierite-filled tube. Silicon(IV) chloride (85 g.; 0.5 mol) is added to the suspension over a 5-minute period with rapid stirring. The reaction is only slightly exothermic. After gentle refluxing for 3 hours, during which vigorous stirring is maintained, the pale yellow mixture is cooled to about 70° and filtered (*hood!*) through a coarse-grade sintered-glass funnel. The solids are washed with five 60-ml. portions of hot benzene, or until the characteristic odor of the isothiocyanate can no longer be detected. The pale yellow filtrate is distilled through a 50-cm. Vigreux column to a residual volume of approximately 200 ml. The hot contents are immediately transferred to a 400-ml. beaker (*hood!*) and the flask rinsed with about 20 to 30 ml. of fresh benzene, which is then added to the main solution. On cooling (in a partially evacuated desiccator to prevent partial hydrolysis of the isothiocyanate by atmospheric moisture), silicon tetraisothiocyanate crystallizes from the concentrated benzene solution. The colorless crystals are filtered rapidly through a coarse-grade sintered-glass funnel, washed with 50 ml. of cold anhydrous sodium-dried benzene, pressed, and drained. Residual benzene is removed by placing the crystals in a vacuum desiccator and evacuating for one hour. The yield of silicon tetraisothiocyanate is 104 to 112 g. [80 to 86% based on silicon(IV) chloride]. An additional 10% of less pure isothiocyanate may be obtained by evaporating the mother liquor to dryness in a rotary evaporator.

When silver thiocyanate is employed in the above preparation, the resulting silicon tetraisothiocyanate is yellow. Silicon tetraisothiocyanate freshly prepared from ammonium thiocyanate is colorless, although on standing for several days the product assumes a pale yellow color.

C. METHYLSILICON ISOTHIOCYANATES

The three possible methylsilicon isothiocyanates are prepared by allowing the appropriate methylchlorosilanes to react with a 25% excess of ammonium thiocyanate in the same equipment and by the same procedure as employed in the synthesis of silicon tetraisothiocyanate. Crystalline methylsilicon triisothiocyanate can be isolated by filtration. Dimethylsilicon diisothiocyanate is isolated by distilling the benzene solution through a 50-cm. Vigreux column and collecting the fraction boiling at 60 to 66° at 1.0-mm. pressure (most of the product distills at 64° at 1.0 mm. pressure). Trimethylsilicon isothiocyanate is obtained by collecting the fraction boiling at 138 to 145° at 760 mm. pressure. The yields of methylsilicon isothiocyanates are: methylsilicon triisothiocyanate, 83%; dimethylsilicon diisothiocyanate, 86%; and trimethylsilicon isothiocyanate, 80%.

Properties

When freshly prepared from ammonium thiocyanate, silicon tetraisothiocyanate is a stable colorless crystalline solid which melts at 143.8° and boils at 313°. It is soluble in chloroform, carbon tetrachloride, acetone, benzene, and petroleum naphtha.

Silicon tetraisothiocyanate is rapidly hydrolyzed to gelatinous silica and thiocyanic acid on exposure to moist air or water. With primary or secondary aliphatic or aromatic amines, silicon tetraisothiocyanate reacts to produce *N*-mono- or *N,N*-disubstituted thioureas, respectively, in essentially 100% yields.[12]

In chemical reactions and physical properties the methylsilicon isothiocyanates are very similar to silicon tetraisothiocyanate. Methylsilicon triisothiocyanate* and dimethylsilicon diisothiocyanate are colorless solids at room temperature, whereas trimethylsilicon isothiocyanate is a colorless liquid. All possess pungent odors and are lacrimators. The melting and boiling points are respectively: methylsilicon triisothiocyanate, 72.4°, 266.8°; dimethylsilicon diisothiocyanate, 18.0°, 217.3°; trimethylsilicon isothiocyanate, −32.8°, 143.1°.

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* Like silicon tetraisothiocyanate, methylsilicon triisothiocyanate turns pale yellow on standing.

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8. TETRAPHENYLGERMANE AND HEXAPHENYLDIGERMANE

Submitted by Frank Glockling* and K. A. Hooton*
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A. TETRAPHENYLGERMANE

$$GeCl_4 + 4C_6H_5MgBr \xrightarrow{\text{tetrahydrofuran}} (C_6H_5)_4Ge + 2MgCl_2 + 2MgBr_2$$

The following procedure,[1] using tetrahydrofuran as solvent, is simpler and gives a higher yield of product (85%) than earlier methods.[2] Complete removal of excess magnesium is essential to avoid the formation of hexaphenyldigermane as a by-product.

Procedure

Phenylmagnesium bromide solution [resulting from the reaction of 88 g. (0.56 mol) of bromobenzene with 15.6 g.

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